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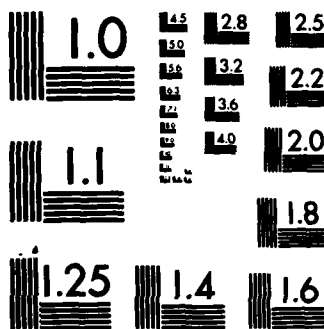
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18. SUPPLEMENTARY NOTES

PVF₂ or poly(vinylidene fluoride), piezoelectric, pyroelectric

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Plasticized and unplasticized, unoriented phase II PVF₂ films were poled at fields ranging from 0.5 MV/cm to 1.25 MV/cm at room temperature for 10 minutes. X-ray diffraction data revealed that at fields near 1.0 MV/cm, a change in conformation to produce phase I occurred. The amount of phase I produced was found to be significantly higher in the case of plasticized film. The plasticized films also showed higher piezoelectric strain coefficient, d₃₁, stress coefficient, e₃₁, and pyroelectric coefficient py, as compared to unplasticized films subjected to

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20. ABSTRACT (continued)

identical poling conditions. In a similar study of oriented phase I films (obtained by stretching plasticized and unplasticized phase II films), poling fields ranging from 0.5 MV/cm to 2.0 MV/cm were used. The Bragg angle for the (110), (200) reflection and the half-width for this reflection were found to be higher for the poled plasticized films with 2θ increasing with increasing plasticizer content. P_y , e_{31} , and d_{31} were also higher as compared to the unplasticized films.



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Technical Report No. 3

THE EFFECT OF PLASTICIZER ON THE POLARIZATION OF
POLY(VINYLDENE FLUORIDE) FILMS

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ABSTRACT

Plasticized and unplasticized, unoriented phase II PVF₂ films were poled at fields ranging from 0.5 MV/cm to 1.25 MV/cm at room temperature for 10 minutes. X-ray diffraction data revealed that at fields near 1.0 MV/cm, a change in conformation to produce phase I occurred. The amount of phase I produced was found to be significantly higher in the case of plasticized film. The plasticized films also showed higher piezoelectric strain coefficient, d_{31} , stress coefficient, e_{31} , and pyroelectric coefficient p_y , as compared to unplasticized films subjected to identical poling conditions. In a similar study of oriented phase I films (obtained by stretching plasticized and unplasticized phase II films), poling fields ranging from 0.5 MV/cm to 2.0 MV/cm were used. The Bragg angle for the (110), (200) reflection and the half-width for this reflection were found to be higher for the poled plasticized films with θ increasing with increasing plasticizer content. p_y , e_{31} , and d_{31} were also higher as compared to the unplasticized films.

I. INTRODUCTION

The crystal structures of four crystal forms of Poly(vinylidene fluoride) have been reported. The non-polar form II occurs upon cooling from the melt. Form II (α form) has a chain conformation which is TGTG' (trans-gauche-trans-gauche').^{1,2} Subsequent mechanical orientation of form II at temperatures below 50°C yields the polar form I.¹⁻³ The morphology and crystal form can be controlled by other techniques such as crystallization from solution⁴ and high temperature annealing.⁵ Form I (β form) has a planar (all trans) zig-zag conformation. Form III has been found in films cast from Dimethyl Sulfoxide,⁴ and also in pressure-crystallized specimens.^{6,7} Form III (γ form) has a TTTGTTTG' chain conformation.^{2,5,6} A fourth crystal form of Poly(vinylidene fluoride) is obtained by poling films containing form II PVF₂. There were no changes in d-spacings noted between the phase II and phase IV material, leading to the conclusion that the phase IV unit cell has dimensions similar to the phase II unit cell.^{2,8} The existence of a fifth crystal form has been proposed on the basis of additional X-ray reflections which appear following the poling of form II PVF₂ with very high fields at room temperature.⁹

Changes in molecular conformation of PVF₂ can occur during mechanical stretching or film polarization. Orientation of the polymer chains, with a conversion to form I can be achieved by uniaxial or biaxial stretching at low temperatures.^{1,2} Increasing the draw temperature results in a decrease in the amount of conversion. The piezoelectric activity is enhanced by stretching or rolling the film prior to poling.^{9,11} Treatment of the PVF₂ films by poling in a high D.C. electric field also gives rise to various crystal transitions.¹²

Oriented phase I films have the greatest piezoelectric activity.

A model has been proposed in which polarization of these films has been related to dipole reorientation within the phase I crystallites.¹³

The phase I crystal structure certainly indicates a very high dipole moment per unit volume as compared with other polymers. Field-induced dipole reorientation can occur for both phase I and phase IV crystal forms.^{14,15} It has been shown that the initial crystallite orientation with respect to poling field direction is important both to the poling mechanisms available and to the resulting piezoelectric properties.⁹

Burkard and Pfister,¹⁶ Sussner¹⁷ and Ohigashi¹⁸ demonstrated that a large piezoelectric effect could be obtained from PVF_2 originally in the phase II crystalline form. Das Gupta and Doughty¹⁹ and Davis et al.⁸ reported that crystal structure changes could be induced in oriented phase II films by a corona-charging technique. At lower voltage, a new phase with unit cell dimensions identical to those of the phase II unit cell but with a different molecular packing was reported. It was suggested that by a reorientation of PVF_2 chains about their axes under the action of high electric fields a "Polar" phase II was produced. At the highest poling voltages, a transformation to phase I was observed. Newman et al.²⁰ have shown that large piezoelectric activity in phase II PVF_2 films can be induced by high poling fields at room temperature. Their X-ray diffraction data agrees well with the suggestion made by Davis et al.⁸ regarding phase transitions induced by poling fields.

Preliminary studies in our laboratories indicated that addition of plasticizer to the films before poling has a strong influence on the piezoelectric and pyroelectric properties.²¹ Both d_{31} and e_{31} increased for plasticized films under identical poling conditions. Studies of the

effects of absorbed water²² on d_{31} of poled Nylon 11 and Nylon 7 films showed that d_{31} increased with increasing water content. It should be noted that water acts as a plasticizer for Nylons. In order to determine whether or not the presence of plasticizer affects the poling behaviour of the crystalline regions (and not just the amorphous regions) of PVF₂ we studied the X-ray changes associated with field induced phase changes and crystallite reorientation for unplasticized and plasticized PVF₂ films at various poling fields.

We examined uniaxially oriented phase I films and unoriented phase II films (these are initial film orientations). X-ray studies were made before and after poling to observe the field-induced crystal changes occurring in these films.

II. EXPERIMENTAL

Sample Preparation

Unoriented phase II PVF₂ films were made by heating 12 μ m Kureha capacitor grade PVF₂ films between Aluminum foils to 205°C and crystallizing by slow cooling to room temperature. Film thickness was measured to be \sim 30 μ m. For plasticization, the films were immersed before poling in Tricresyl phosphate (80% para and 20% meta) at 130°C. For a 24 hr immersion time, the plasticizer content was found to be 5.50% by weight.

Oriented phase I (plasticized and unplasticized) films were obtained from phase II (plasticized and unplasticized) films by uniaxial stretching in an Instron tensile testing machine. The extension rate was 0.05"/min. and the temperature was 54°C. The plasticizer content was found to be the same before and after stretching. A stretch ratio of 4.4:1 was used for both the plasticized and unplasticized films.

Poling

Unoriented phase II (plasticized and unplasticized) films were placed in the poling apparatus between two polished copper plates connected to a high voltage d.c. supply which was then placed under high vacuum ($\sim 10^{-5}$ torr) and the samples poled at 0.5 MV/cm to 1.25 MV/cm at room temperature. The film surface was coated with silver paint to provide sample electrodes. Oriented phase I (plasticized and unplasticized) films were poled in a similar way. The poling was carried out at 0.5 MV/cm to 2.0 MV/cm at 75°C for 10 minutes. The plasticizer content was found to be the same before and after poling.

Electrical and Mechanical Measurements

The piezoelectric strain constant, d_{31} , piezoelectric stress constant e_{31} , dielectric constant and modulus were measured in a Toyo-Seiki Piezotron at 3 Hz. The film surfaces were coated with a thin layer of soft silver epoxy to serve as electrodes for the electrical measurements. The pyroelectric coefficient, P_y was measured by placing a sample between two copper plates connected to an electrometer. The sample was then placed in a temperature controlled chamber. Currents were measured for both heating and cooling cycles at a constant controlled rate of 3°C/min. The pyroelectric coefficient was calculated for room temperature.

X-ray Studies

A quantitative measure of the amount of phase I material produced by poling the initially unoriented phase II films (unplasticized and plasticized) was obtained from the wide-angle diffraction scans shown in Fig. 1 and Fig. 2, using Cu K α radiation. Diffraction scans taken in the transmission mode showed no phase I reflections, showing that the

phase I produced on poling was oriented. A quantitative measure of the fractional content of phase I and phase II was determined from the reflection diffraction scans by taking the ratio of the area under the phase I or phase II peaks to the area under all the crystalline diffraction peaks. The assignment of diffraction peaks to the phase I or phase II crystal forms was based on previous crystallographic studies.^{1,3} Since phase I was oriented, volume ratios of phase I to phase II obtained by these measurements do not provide absolute values. However, this quantitative data can be used for comparative studies. The diffractometer scans were also used to determine the half width for the (110), (200) phase I reflections for both the plasticized and unplasticized uniaxially oriented films. Diffraction scans were also taken for the oriented phase I films after heat treatment in the poling apparatus under identical conditions to poling (without applying the poling field) to separate the effects of thermal annealing. X-ray photographs were also taken on flat film with the X-ray beam perpendicular to and parallel to the plane of the PVF₂ films both before and after poling. No additional crystal forms other than phases I and II are observed.

III. RESULTS AND DISCUSSION

Unoriented Phase II Films

The diffractometer scans (reflection mode) for both the unplasticized and plasticized phase II PVF₂ films before and after poling are shown in Fig. 1 and Fig. 2. All these samples were poled at room temperature for 10 min. Fig. 3 shows a representation of the X-ray diffraction patterns obtained with the X-ray beam parallel to the plane of the film (unpoled, unoriented phase II). Figs. 4 and 5 show representations

of the X-ray diffraction patterns for the unplasticized and plasticized films after poling at 1.25 MV/cm (beam parallel to the plane of the film).

The strong influence of the plasticizer on the field-induced phase transformation from II to I can be easily seen by comparing Fig. 1 and Fig. 2. The most intense (110) (200) reflection for phase I is seen as a shoulder on the phase II (110) peak in Fig. 2. It is not nearly as prominent for the unplasticized film even at 1.25 MV/cm (Fig. 1). It can also be seen in Fig. 5 as a shoulder on the (110) phase II reflection, with the arc centered on the meridional position indicating that the phase I produced is highly oriented, but in Fig. 4 (unplasticized) it is not clearly seen.

The piezoelectric and pyroelectric coefficients of the unplasticized and plasticized films are shown in Table 1. The plasticized sample has a d_{31} of 2.8 PC/N and a pyroelectric coefficient, P_y of $11.6 \mu\text{Cm}^{-2} \text{K}^{-1}$ compared to a d_{31} of 2.1 PC/N and a P_y of $10.4 \mu\text{Cm}^{-2} \text{K}^{-1}$ for the unplasticized film poled under identical conditions.

The above results can be interpreted as showing that for plasticized samples, the initially non-polar phase II crystal form film has been more easily polarized and a phase transformation to the polar phase I has taken place at much lower poling fields than observed earlier for unplasticized samples.^{14,15} Initially, the phase II crystallites were unoriented, as is clear from Fig. 3. Since all crystals with a particular orientation with respect to the applied field direction are equally likely, if crystals with a particular orientation show a crystal phase transformation, both the new phase and the initial phase (with respect to the phase transition) show preferred orientation.⁹ This can be seen by

comparing Fig. 3 and Fig. 5. Fig. 5 shows a decrease of intensity in the meridional direction for the (100) reflection and an increase in intensity for the (200) reflection. Fig. 2 shows that the (100) intensity (in reflection mode) decreases sharply, while the (200) reflection shows an increase. As indicated in Fig. 3 and Fig. 4, we observe a slight increase in the (200) reflection intensity and a slight decrease in the (100) reflection intensity for the unplasticized film. This is also seen in Fig. 1. This behaviour is expected if conversion of phase II (non-polar) to phase IV takes place, as reported by many previous workers.^{2,3,8,14} The principal difference between the diffraction patterns of phase II and phase IV is that for phase IV, the structure factor for the (100) reflection is equal to zero, while for the (200) reflection, the value is increased.⁸ However, since phase II and phase IV have all reflections (d spacings) in common, only some of which differ in intensity, most of the Debye-Scherrer rings will be complete, both phase II and IV contributing to the intensities.⁹

A quantitative estimate of the phase I formed during poling was made for the unplasticized and plasticized films poled at 1.25 MV/cm. The amount of phase I formed for the plasticized films (28%) is significantly higher than the amount of phase I formed in the case of unplasticized films (17%) as shown in Table I. The actual amount of phase I formation differs from these calculated values as the diffractometer scan (reflection model) only records diffracted intensity from planes parallel to the film surface. This may be clearly seen in the (110), (200) arc on the X-ray photographs represented in Fig. 5. Also, since the dipole direction of phase I is along the crystallographic b axis, this observed intensity should result from the (110) reflection.

Oriented Phase I Films

The diffractometer scans for oriented phase I films (unplasticized and plasticized) in reflection mode are shown in Fig. 6 and Fig. 7 respectively. The transmission scans for the above films are shown in Fig. 8 and Fig. 9. Reflection and transmission scans for unpoled films with the same thermal history as that of the poled samples are also shown in these figures. Table 2 shows the 2θ values and half widths for the composite (110)(200) reflection of phase I under various conditions. It is clearly seen that the 2θ value for the poled plasticized sample (20.85°) is greater than that for the poled unplasticized sample (20.7°). The shift in 2θ value may indicate a decrease in interplanar separation caused by better packing. However, neither the heat treatment alone or poling unplasticized film gave rise this effect which was observed only for the poled plasticized films. Thus we believe is more likely it may be due to field induced preferential reorientation of crystallites as shown in Fig. 10, (based on the pseudohexagonal model, and crystal structure determination of Hasegawa et al.⁷). The 2θ value for the (110) reflection is slightly higher than that for the (200) reflection: 2θ for (110) = 20.72° and 2θ for (200) = 20.63° .

It is important to remember that hkl reflections observed in the diffraction scan taken in reflection mode all originate from crystals with (hkl) planes parallel to the surface of the film. The (110)(200) composite peak which shows the shift in Bragg angle thus originates from crystals with two distinct orientations with respect to the film normal (and thus the applied field during poling. The (200) reflection originates from crystals with the a-axis perpendicular to the film

surface (lattice orientations (2)) while the (110) reflection originates from crystals with lattice orientation (3). We would not expect a lattice re-orientation under field to occur for crystals with orientation (3) since the dipole moments are $\sim 30^\circ$ with respect to the applied field. A switching of 180° for those crystals in the wrong direction would show no change in the X-ray diffraction intensities. However for crystals with lattice orientation (2), dipole moments are 90° to the applied field during poling. If some re-orientation of these crystals took place, the intensity of (200) reflection ($d = 4.30 \text{ \AA}$) would decrease, thus shifting the centre of gravity of the composite peak closer to the peak of the (110) reflection ($d = 4.28 \text{ \AA}$). The observed shift in Bragg angle is approximately the correct value, and in the correct direction for this to be a plausible explanation. Apparently this polarisation mechanism cannot take place under these poling conditions in the absence of plasticizer. The increase in the 2θ value is also observed for different plasticizer content (Fig. 11) with the $\Delta 2\theta$ value increase with increasing plasticizer content. The (001) reflection in transmission mode does not show any change in 2θ values with poling for either the unplasticized or the plasticized films as shown in Fig. 8 and Fig. 9. This indicates that the poling induced changes occur only in directions transverse to the chain-axis in the crystallites.

Comparing the half widths of the reflections from both the plasticized and unplasticized films before and after poling and also after only heat-treatment indicate that unpoled samples without the heat treatment have the greatest half widths and the poled samples the least. The half-width for the (110)(200) reflection in the unplasticized films decreased

from 0.027 radians (unpoled) to a value of 0.0225 radians for the poled sample. The value for the heat treated sample is 0.0245 radians. In the case of the plasticized films, the corresponding values decrease from 0.0305 radians (unpoled) to 0.027 radians (poled), the value for heat treated samples being 0.0285 radians. The decrease in half width for heat treated and poled (both plasticized and unplasticized) as compared to untreated samples may be due to annealing effects resulting in increased perfection of the crystallites. In each of the three cases (unpoled, heat treated, and poled), the half widths are greater for the plasticized samples as compared to the unplasticized samples. No such changes in half widths are observed for the (001) reflection. There is no significant change in the crystallinity of the samples. The increase in the half width for the (110)(200) reflection with plasticization suggests that the plasticizer may be diffusing into the crystalline regions of the samples, only from the top and bottom surfaces of the crystallites between the folded chains and thus not affecting the (001) reflection. As recently suggested by Reneker et al.,²³ field induced reorientation of phase I crystals may occur from the bottom to the top of a crystal (bottom to top of the molecular stems) by propagation of a twist layer. The twist layer would then be the domain wall separating the reoriented from the not as yet reoriented domain. Such a process might be facilitated by the presence of plasticizer between the molecular stems near and at the crystal surface.

The piezoelectric and pyroelectric constants for the films poled at 2 MV/cm are shown in Table 3. The plasticized film shows higher d_{31} (25.8 PC/N), higher e_{31} (60 mC/m²) and higher pyroelectric constant,

P_y ($28.2 \text{ Cm}^{-2}\text{K}^{-1}$) compared to unplasticized films ($d_{31} = 23 \text{ PC/N}$; $e_{31} = 50.5 \text{ mC/m}^2$; $P_y = 24.5 \text{ Cm}^{-2}\text{K}^{-1}$). The dielectric constant for the plasticized film (14.85) is also higher than that for the unplasticized film (12.15). The modulus of the plasticized films ($2.15 \times 10^{10} \text{ dynes/cm}^2$) is significantly lower than that of the unplasticized films ($2.4 \times 10^{10} \text{ dynes/cm}^2$) which is quite expected with plasticization since the T_g for the plasticized sample is lower (-53°C) than that of the unplasticized films (-41.8°C).

IV. CONCLUSION

Previous studies have shown that there are various stages of field-induced crystal transitions in phase II PVF_2 . At relatively lower fields, the non-polar phase II converts to polar phase II (phase IV) by reorientation of chains about their axes and this is reflected in the increasing piezoelectric and pyroelectric response. At higher fields, phase I is formed. In the present study, we observed similar phase transitions for the plasticized PVF_2 films but the transitions take place at much lower poling fields as compared to unplasticized films under similar conditions. We also observed that the amount of phase I formed is much greater in the case of plasticized films as compared to unplasticized films under identical poling conditions.

In the case of oriented phase I films, plasticization leads to an increase in piezoelectric and pyroelectric response. The increase in 2θ values for the composite (110)(200) reflection with plasticization indicates that the (110) planes may be preferentially aligning parallel to the plane of the film. As the 2θ value for the (110) reflection

is larger than that of the (200), the 2 θ for the composite (110)(200) peak increases. The increase in half width for the (110)(200) reflection with plasticization indicates that the plasticizer is diffusing into the crystalline regions. Since there is no change in the half width for the (001) reflection with plasticization, the plasticizer may be diffusing in from the top and bottom surfaces of the crystallites between the folded chains and thus leaving the (001) reflection unaffected. If the field induced reorientation of the molecular stems first occurs at the region where the stems enter or exit the crystal as suggested by Keneker et al.,²³ plasticizer should facilitate the process.

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FIGURE CAPTIONS

- Fig. 1. Diffractometer scan (reflection mode) of unoriented PVDF film subjected to different poling fields.
- Fig. 2. Diffractometer scan (reflection mode) of plasticized unoriented PVDF film subjected to different poling fields.
- Fig. 3: Representation of the X-ray diffraction pattern from the unpoled unoriented PVF₂ film taken with the X-ray beam in the plane of the PVF₂ film.
- Fig. 4: Representation of the X-ray diffraction pattern from the poled (initially unoriented) PVF₂ film taken with the X-ray beam in the plane of the PVF₂ film: $E_p = 1.25$ MV/cm.
- Fig. 5: Representation of the X-ray diffraction pattern from the plasticized poled (initially unoriented) PVF₂ film taken with the X-ray beam in the plane of the PVF₂ film: $E_p = 1.25$ MV/cm.
- Fig. 6: Diffractometer scan (reflection mode) of uniaxially oriented PVDF film.
- Bottom scan - unpoled
- Middle scan - subjected to poling thermal cycle (no field)
- Top scan - poled at 2 MV/cm
- Fig. 7: Diffractometer scan (reflection mode) of plasticized uniaxially oriented PVDF film.
- Bottom scan - unpoled
- Middle scan - subjected to poling thermal cycle (no field)
- Top scan - poled at 2 MV/cm.

Fig. 8: Diffractometer scan (transmission mode) of uniaxially oriented PVDF film.

Bottom scan - unpoled

Middle scan - subjected to poling thermal cycle (no field)

Top scan - poled at 2 MV/cm

Fig. 9: Diffractometer scan (transmission mode) of plasticized uniaxially oriented PVDF film.

Bottom scan - unpoled

Middle scan - subjected to poling thermal cycle (no field)

Top scan - poled at 2 MV/cm

Fig. 10: Orientations of phase I crystals with respect to poling field (film normal).

Fig. 11: Variation of shift in Bragg angle with plasticizer content.

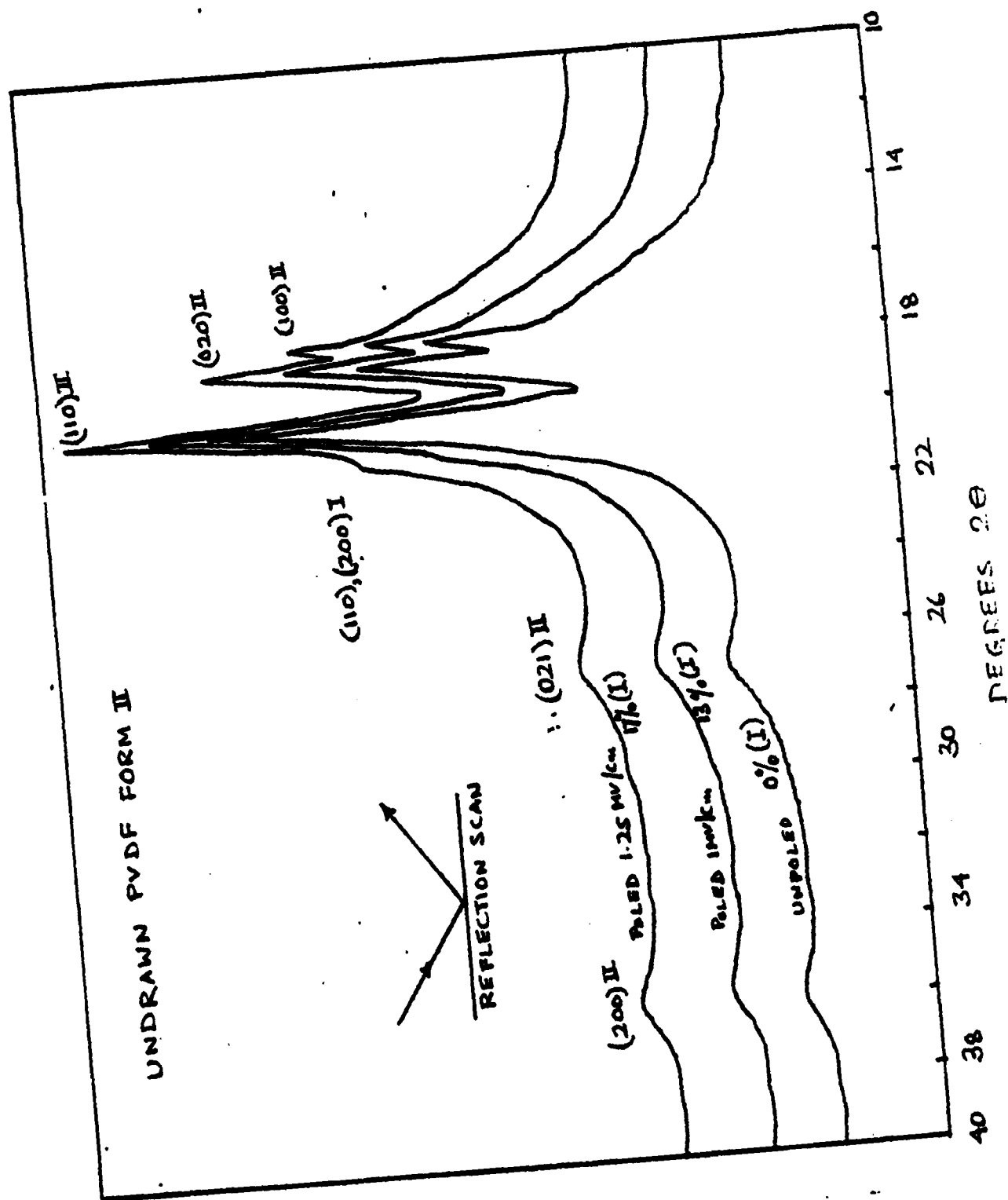


FIGURE 1

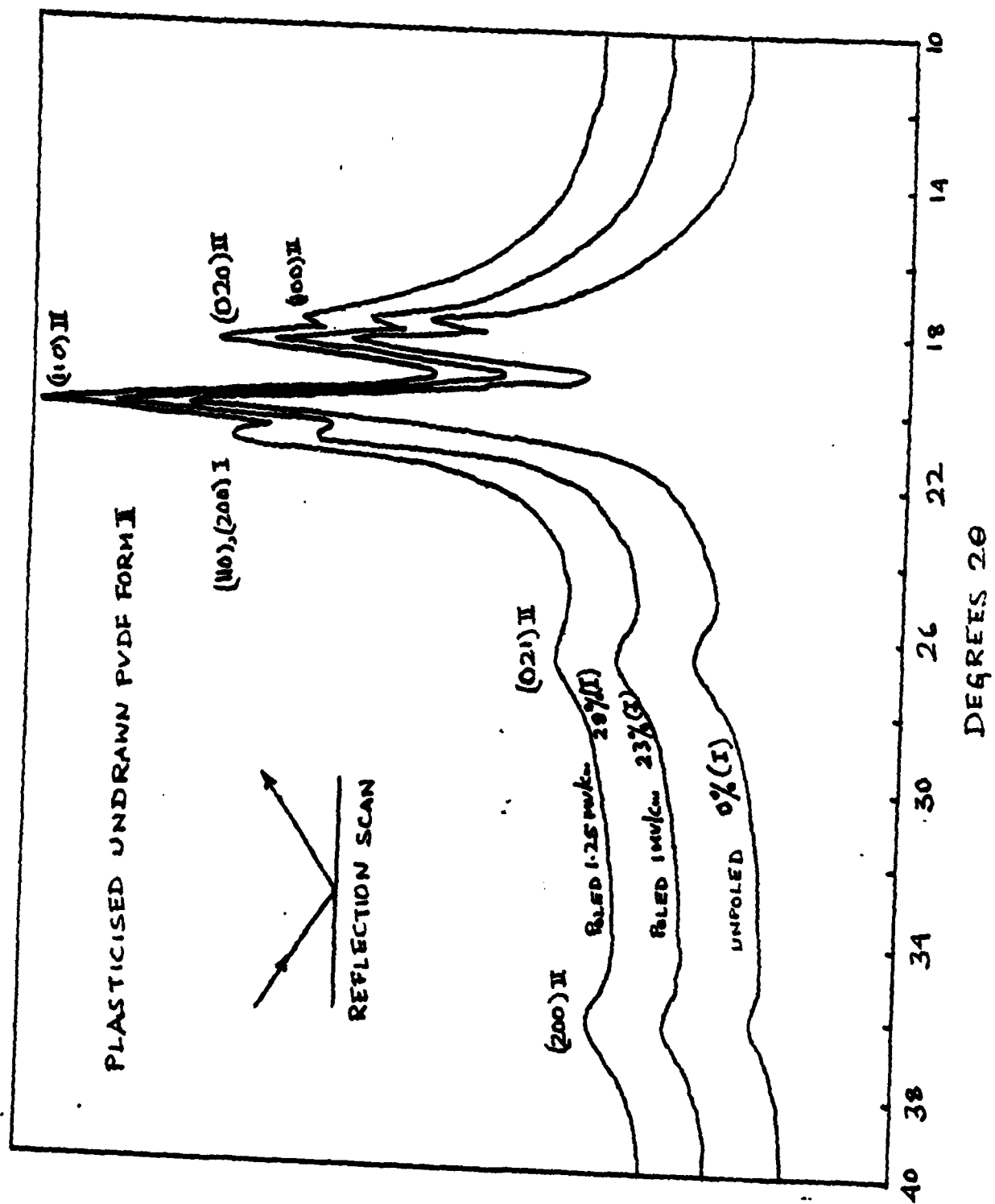


FIGURE 2

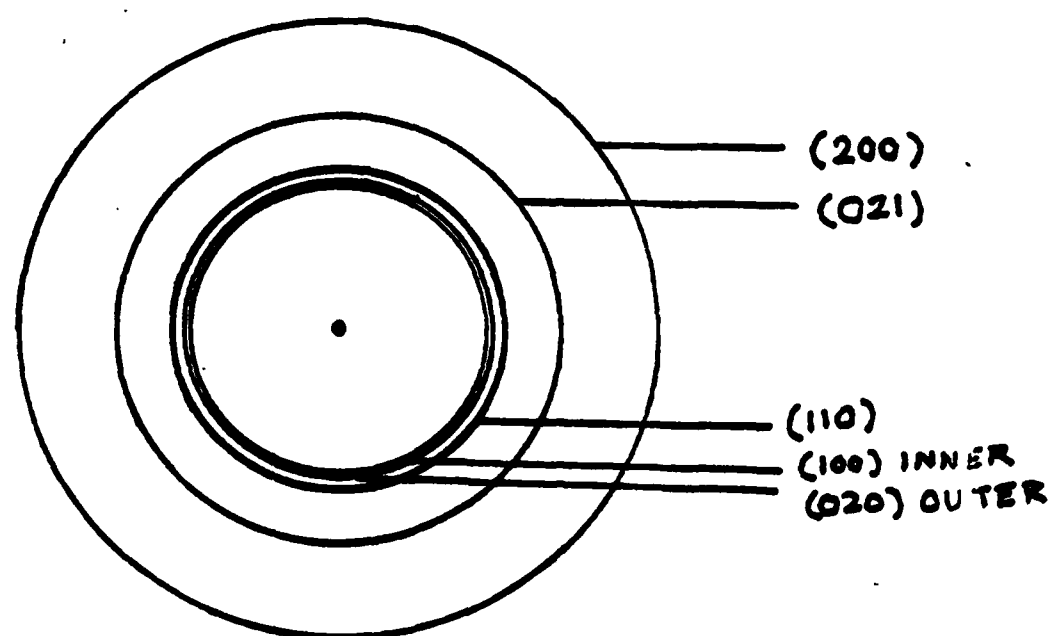


FIGURE.3

X-ray diffraction pattern, with beam parallel
to plane of unpoled unoriented PVF_2 film.

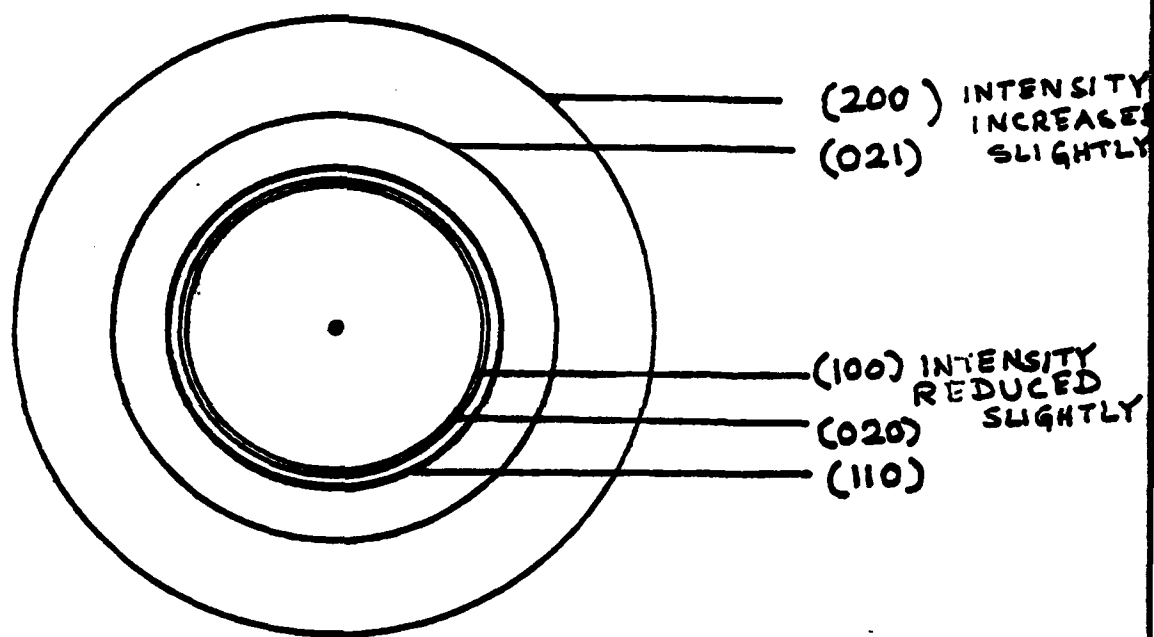


FIGURE.4

x-ray diffraction pattern, with beam parallel to plane of poled PVF_2 film. The poling field was 1.25 MV/cm .

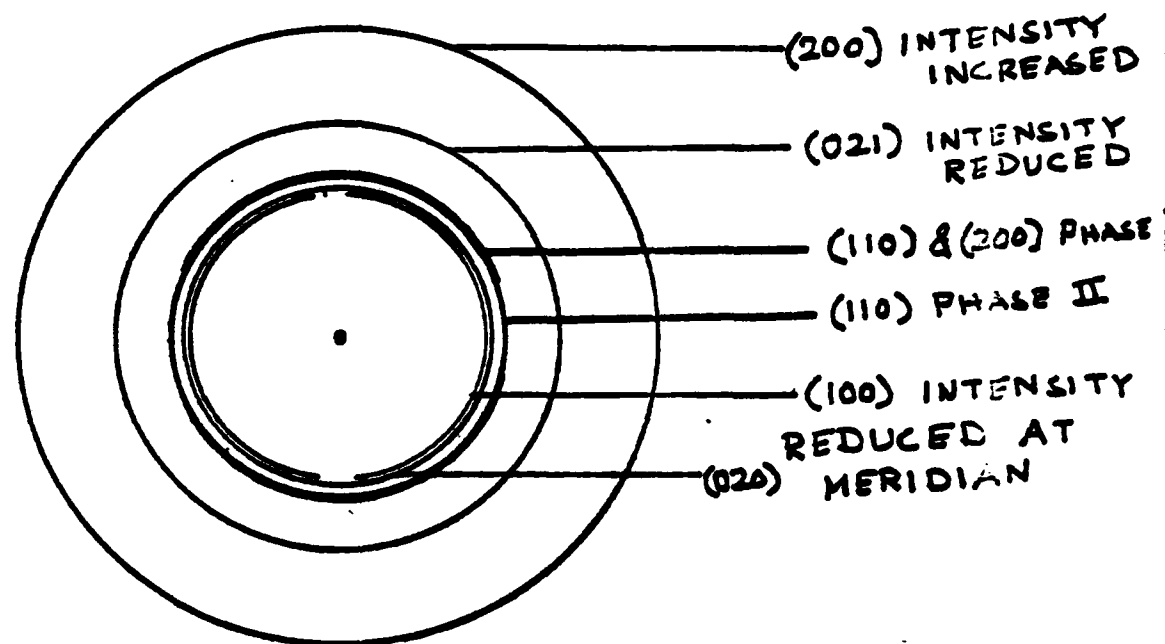


FIGURE. 5

x-ray diffraction pattern, with beam parallel to plane of plasticised, poled PVF₂ film.
The poling field was 1.25 MV/cm.

TABLE-1

	d_{31} (pc/N)	ϵ_{31} (mc/m ²)	P_g ($\mu\text{Cm}^{-2}\text{OK}^{-1}$)	Dielectric Constant	Modulus ($\times 10^{10}$ dyn/cm ²)	Phase I formed (%)
Unplasticised (Poled 1.25 MV/cm)	2.1	4.1	10.4	12.10	2.15	17
Plasticised (Poled 1.25 MV/cm)	2.8	4.7	11.6	14.20	1.75	28

DRAWN PVDF FORM I

(110), (200) I

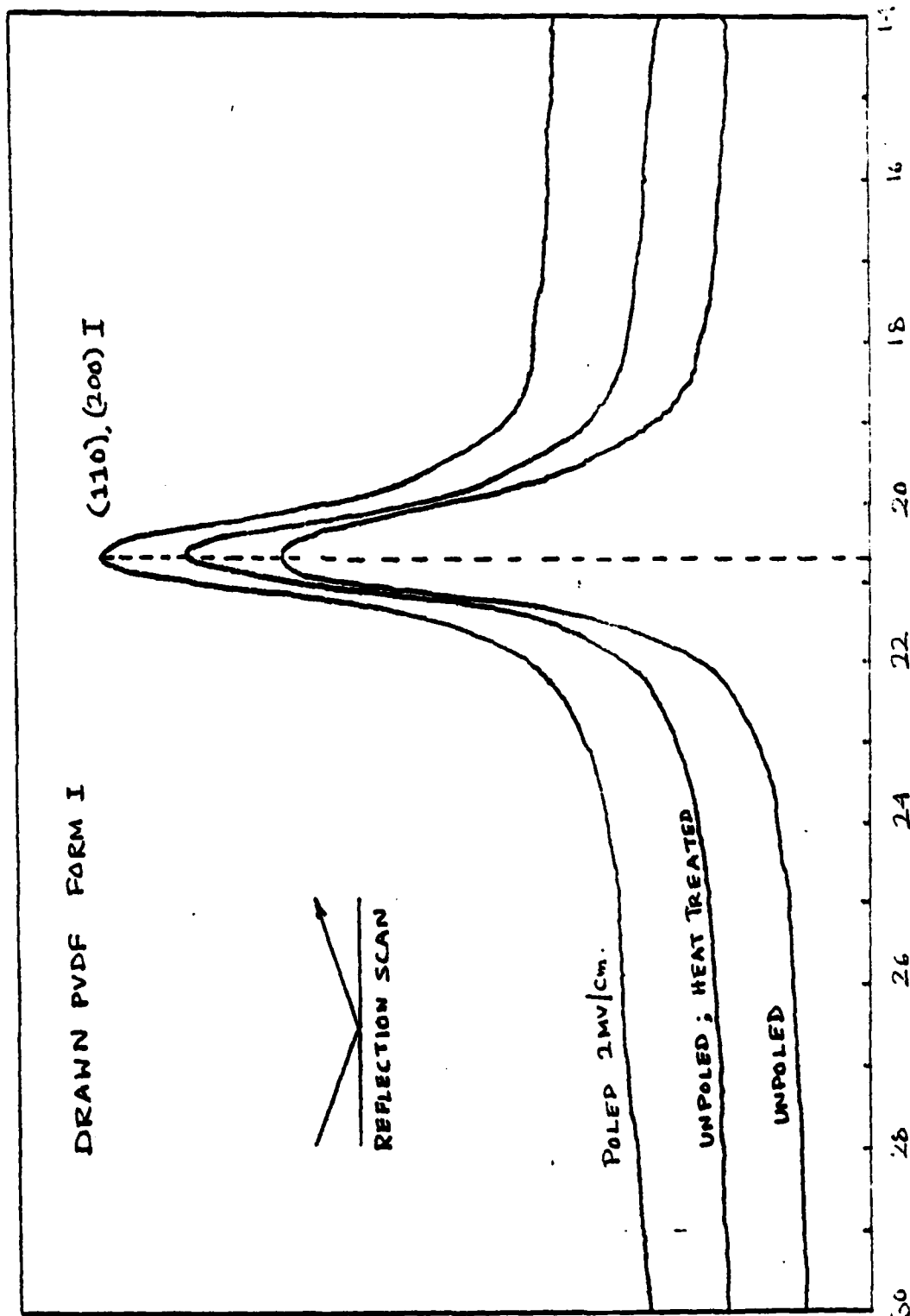
REFLECTION SCAN

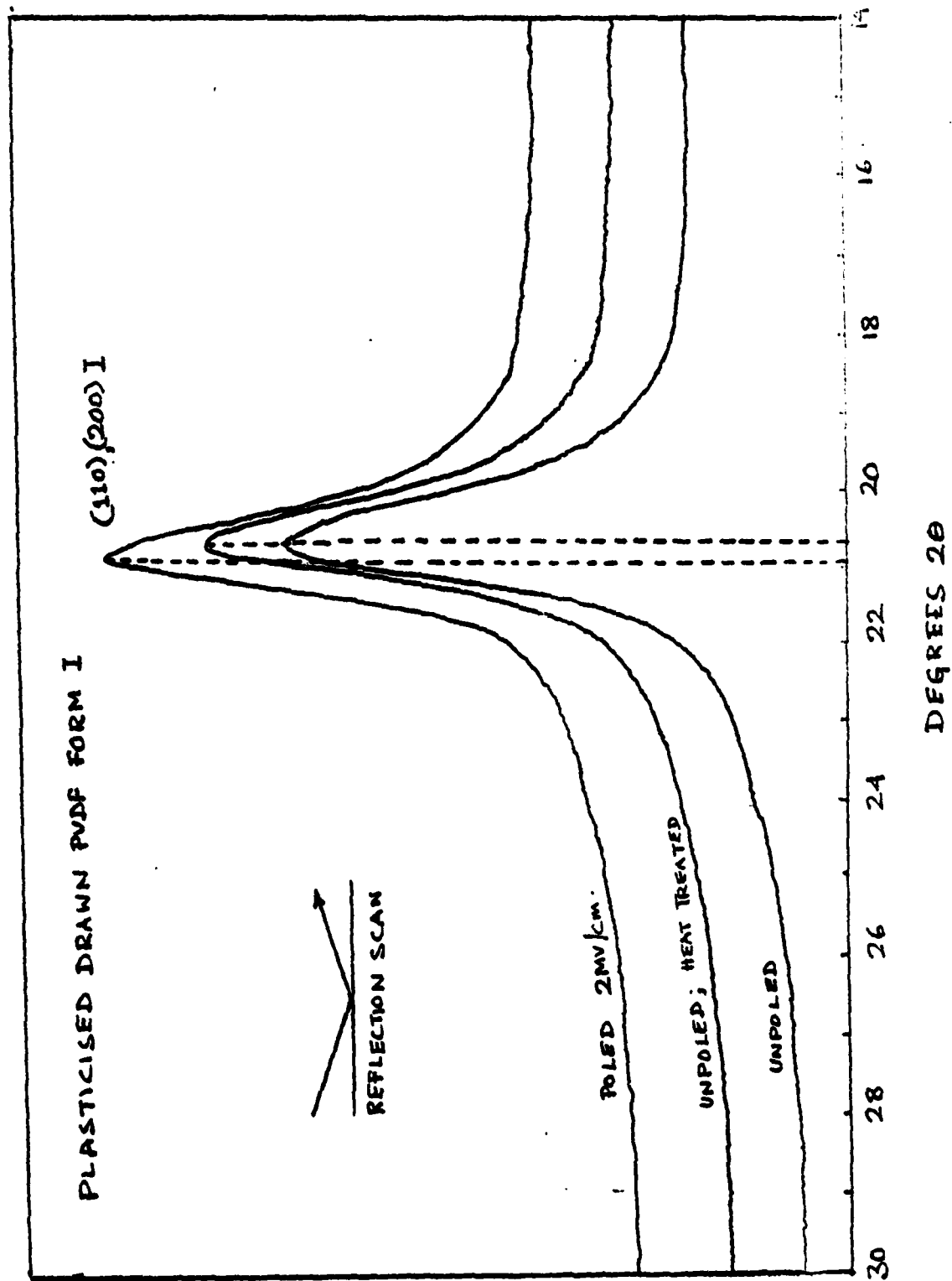
POLED 2MV/CM.

UNPOLED; HEAT TREATED

UNPOLED

DEGREES 2θ





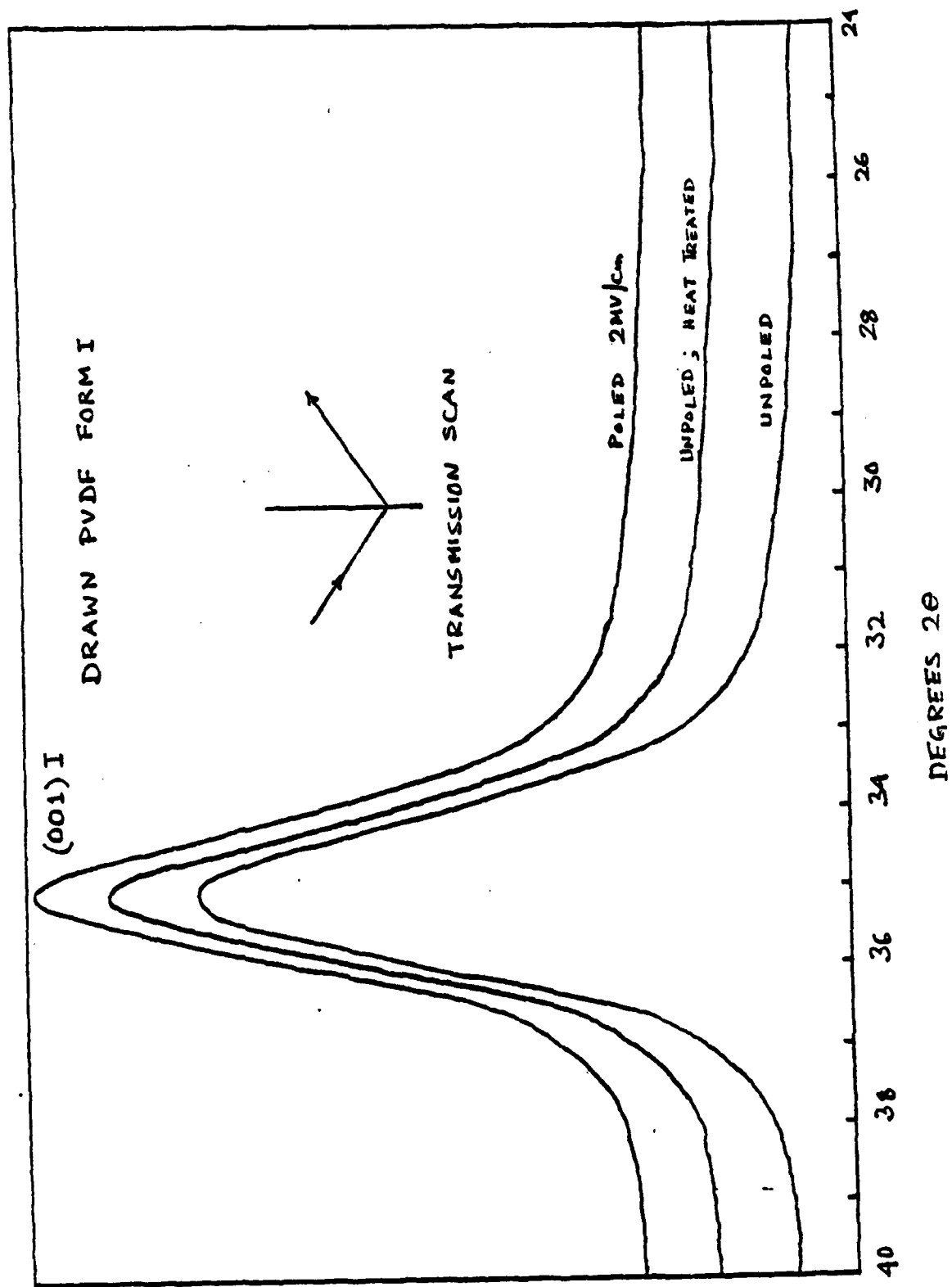
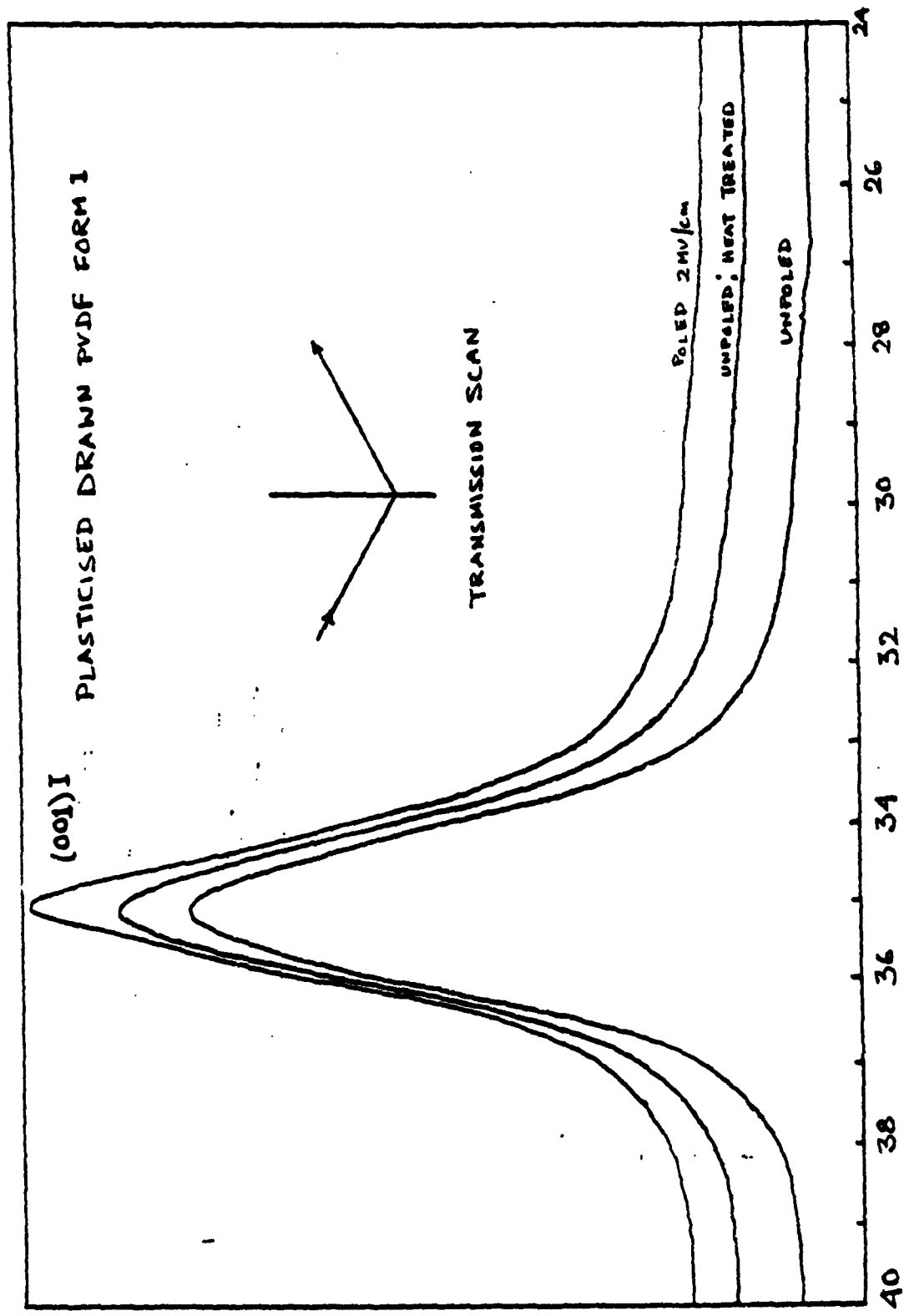
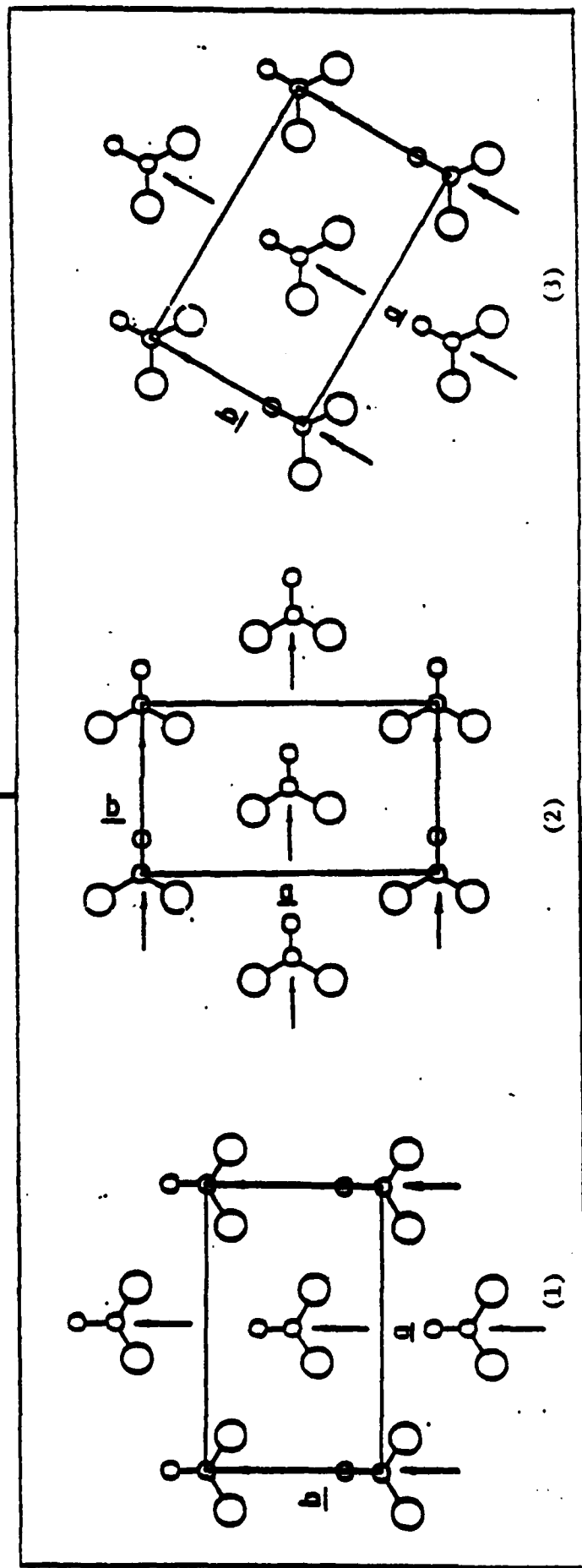


FIGURE-8



↑ Film Normal



The crystal structure of phase I Poly(vinylidene fluoride)
determined by Hasegawa et. al.

$$a = 8.58^{\circ}\text{A}, b = 4.91^{\circ}\text{A}, c = 2.56^{\circ}\text{A}$$

$$d_{110} = 4.28^{\circ}\text{A}, (2\theta = 20.72^{\circ})$$

$$d_{111} = 4.30^{\circ}\text{A}, (2\theta = 20.63^{\circ})$$

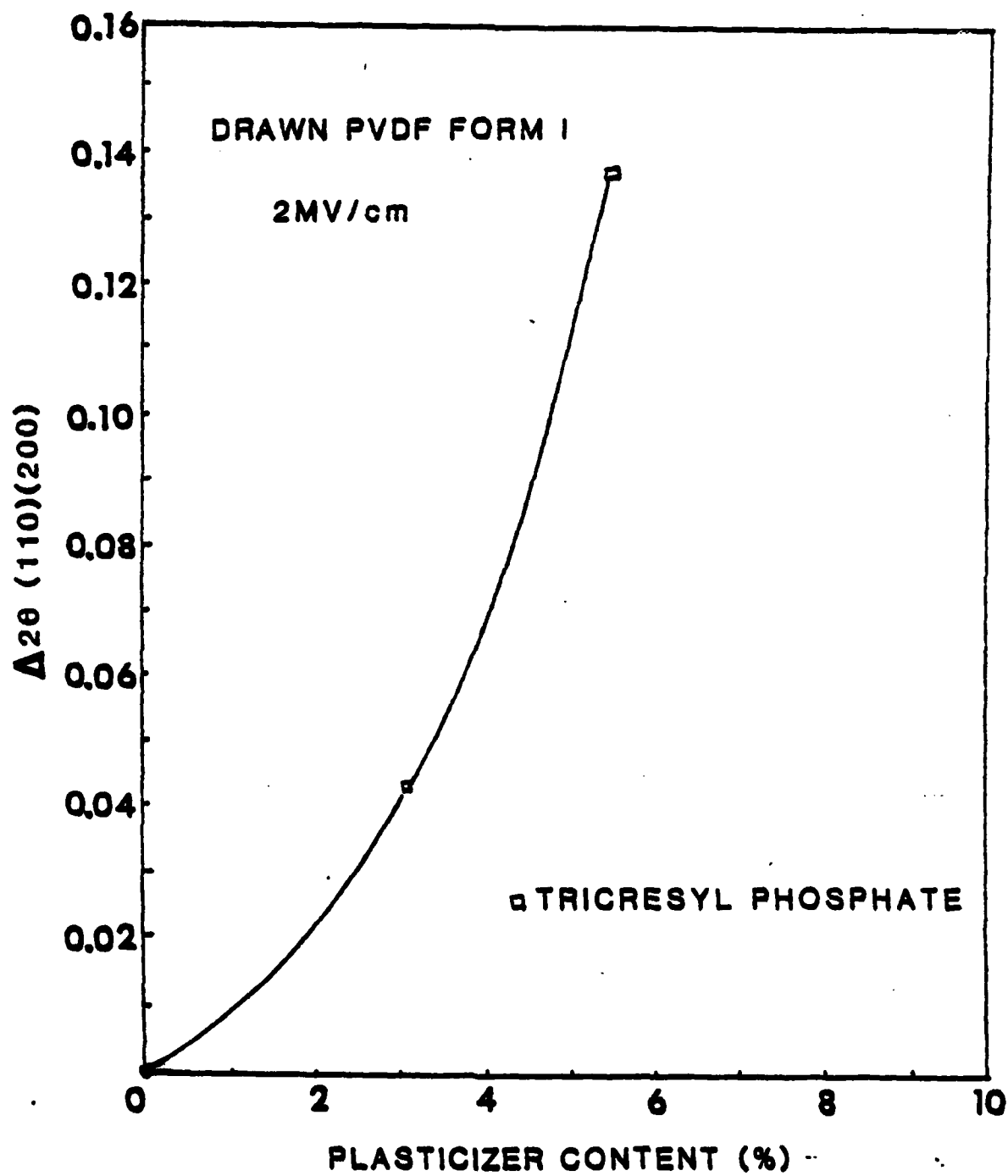


FIGURE 11

TABLE-2

	UNPLASTICISED			PLASTICISED		
	Unpoled	Heat Treated	Poled 2MV/cm	Unpoled	Heat Treated	Poled 2MV/cm
2θ	20.7	20.7	20.7	20.7	20.7	20.25
$\beta_{\frac{1}{2}}$ (radians)	0.0270	0.0245	0.0225	0.0305	0.0285	0.0270

TABLE-3

	d_{31} (pC/N)	e_{31} (mC/m ²)	P_g ($\mu\text{Cm}^{-20}\text{K}^{-1}$)	Dielectric Constant	Modulus ($\times 10^{10}\text{dyn/cm}^2$)
Unplasticised (Poled, 2MV/cm)	23.1	50.5	24.5	12.15	2.40
Plasticised (Poled, 2MV/cm)	25.8	60.0	28.2	14.85	2.15

